HYBRID POLYMER NANOCOMPOSITES: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

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Title of the Thesis**:** **HYBRID POLYMER NANOCOMPOSITES: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS**

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Introduction

Water contamination due to the discharge of untreated effluents of industries into the waterbodies is a serious environmental issue globally [1,2]. The pollutants present in water, even in low concentrations, are damaging to aquatic and terrestrial life. Adsorption is a well-accepted method of wastewater treatment since it is convenient, cost-effective and efficient [3,4]. As adsorbents, a variety of materials have been used, such as, activated carbon, clay minerals, zeolites, coal, sawdust, and biopolymers [5,6]. Among these materials, biopolymers have attracted much attention because of their great abundance, biodegradability, adsorption effectiveness, low cost, and reusability [7].

It has been suggested that a combination of electrostatic interactions, van der Waals forces, and hydrogen bonding between the adsorbent and dye molecules are responsible for the high levels of adsorption exhibited by polysaccharides [8]. It can be further improved by chemical modifications. Graft copolymerization with synthetic monomers is an excellent way of enhancing the adsorption characteristics of polysaccharides [9].

Nanotechnology offers the chance to produce novel substances for efficient wastewater treatment [10,11]. High surface area nanoparticles can make significant improvements in the adsorption process, but their application is constrained by the formation of bigger particles due to agglomeration. Incorporating them into the polysaccharide matrix, however, can reduce agglomeration [12]. If the incorporated nanoparticles possess magnetic nature, the resulting nanocomposite materials will have an additional advantage as adsorbents. On application of an external magnetic field, it would be possible to separate the adsorbents from wastewater after the adsorption process [13].

The present work is on the development of adsorbents based on modification of polysaccharides and by formation of nanocomposites with a magnetic material.

The preparation and characterization of a few polysaccharide based materials modified via graft copolymerization with acrylic monomers and their nanocomposite with magnetic particles (Fe_3O_4) for

the development of novel adsorbents have been presented in this thesis. The graft copolymer hydrogels and their magnetic nanocomposites based on plant waste, Banana Pseudo Stem have been made and evaluated as adsorbents for removal of cationic dyes from aqueous solution. Crystal Violet (CV) and Methylene Blue (MB) have been used as model dyes in the study.

The grafting on the polysaccharide molecules has been carried out by free radical polymerization of monomers namely N-hydroxyethylacrylamide (HEAAm) and 4-acryloylmorpholine (AcM). For polymerization, potassium peroxodisulphate (KPS) has been used as an initiator. In order to create the network, the monomers were polymerized with the crosslinking agent N,N^{1}-methylenebisacrylamide (MBA). Graft copolymer gels were made using the microwave irradiation technique. The magnetic (Fe_3O_4) nanoparticles were embedded in the gels through *in-situ* formation to obtain the corresponding nanocomposites.

Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Vibrating Sample Magnetometer (VSM) have been used to characterize the synthesized hydrogels and their nanocomposites.

The swelling characteristics have been investigated under different pH conditions. The adsorption and desorption experiments have been performed in detail. Using the Langmuir and Freundlich adsorption isotherm models, adsorption data has been examined. Pseudo-first order and pseudo-second-order kinetic models have been employed to study kinetics of adsorption. Studies on thermodynamics have been carried out to comprehend the nature as well as the feasibility of the adsorption process. Desorption tests have been carried out to check the possibility of reuse of adsorbents. The results of the study have been presented and discussed in six chapters as detailed below.

Chapter-1: Introduction

1.1 : Introduction to polysaccharide-based hydrogels
1.2 : Classification of hydrogels
1.3 : Introduction to nanocomposite hydrogels
1.4 : Fabrication of nanocomposite hydrogels
1.5 : Magnetite nanocomposite hydrogels
1.6 : Methods to make Magnetic Hydrogels
1.7 : Introduction to wastewater treatment by adsorption
1.8 : Review of the literature on biopolymer based adsorbents for water purification
1.9 : Aim and objectives of the present study

Chapter -2: Experimental Section

2.1: Materials
2.2: Methods
2.3: Swelling studies
2.4: Dye adsorption studies
2.5: Thermodynamic studies
2.6: Desorption studies

Chapter-3:Synthesis, characterization and dye adsorption studies of Banana Pseudo Stem supported- poly [(4-acryloylmorpholine)] graft polymer (BPS-g-PAcM) hydrogel and its magnetic nanocomposite

3.1: Introduction
3.2: Preparation
3.3: Structural characterization
3.4: Swelling studies
3.5: Dye adsorption studies
3.6: Desorption studies
3.7: Conclusions
References

Chapter-4:Synthesis, characterization and dye adsorption studies of Banana Pseudo Stem supported-poly [(N-hydroxyethylacrylamide)] graft polymer (BPS-g-PHEAAm) hydrogel and its magnetic nanocomposite

4.1: Introduction
4.2: Preparation
4.3: Structural characterization
4.4: Swelling studies
4.5: Dye adsorption studies
4.6: Desorption studies
4.7: Conclusions
References

Chapter-5: Synthesis, characterization, and dye adsorption studies of Banana Pseudo Stem derived Biochar-graft-poly [(N-hydroxyethylacrylamide)] (BPSBC-g- PHEAAm) hydrogel and its magnetic nanocomposite

5.1: Introduction
5.2: Preparation
5.3: Structural characterization
5.4: Swelling studies
5.5: Dye adsorption studies
5.6: Desorption studies
5.7: Conclusions
References

Chapter-6: Synthesis, characterization, and dye adsorption studies of Banana Pseudo Stem derived Cellulose Fiber-graft-poly [(N-hydroxyethylacrylamide)] (BPSCF-g-PHEAAm) hydrogel and its magnetic nanocomposite.

6.1: Introduction
6.2: Preparation
6.3: Structural characterization
6.4: Swelling studies
6.5: Dye adsorption studies
6.6: Desorption studies
6.7: Conclusions
References

Summary and Conclusions

References

Papers under communication

Papers presented in conferences

Chapter -1: General Introduction

It is an introductory chapter which provides a survey of the literature on the modification of polysaccharides for development of adsorbents for wastewater treatment with a focus on graft copolymers and nanocomposites. The use of polysaccharide-based magnetic nanocomposites as adsorbents for removal of cationic dyes from aqueous solution has been described. The review of literature on studies involving Banana Pseudo Stem, Banana Pseudo Stem derived Biochar and Banana Pseudo Stem derived Cellulose Fiber has been presented.

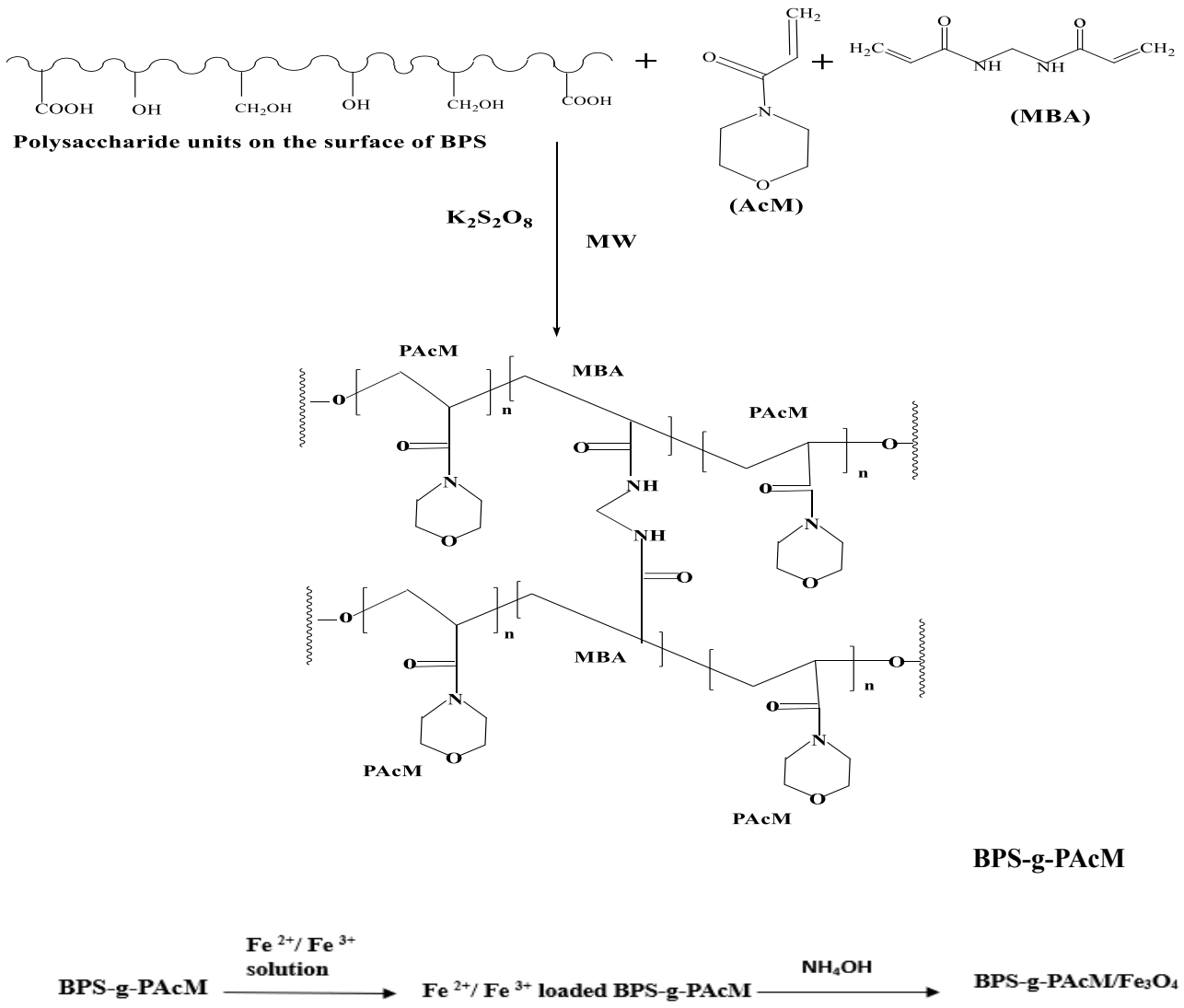
Chapter-2: Experimental Section

This chapter describes the experimental techniques employed for the preparation and characterization of the Banana Pseudo Stem based graft polymer gels and their hybrid nanocomposites. This chapter provides specifics on the materials and techniques utilized for developing hydrogels and nanocomposites. The details of swelling study carried out under different pH conditions have been provided. The methods used for the physicochemical characterization have been presented. The procedure adopted to study the adsorption and desorption process have been provided. The adsorption isotherm models, and kinetic models used to fit the adsorption data have been described. The process of evaluating the thermodynamic parameters of adsorption process has also been presented.

Chapter-3: Synthesis, characterization and dye adsorption studies of Banana Pseudo Stem supported-poly [(4-acryloylmorpholine)] graft polymer (BPS-g-PAcM) hydrogel and its magnetic nanocomposite

The development of Banana Pseudo Stem-graft-poly(4-acryloylmorpholine) hydrogel (BPS-g-PAcM) and its composite material with magnetite, (BPS-g- PAcM/Fe_3O_4) is discussed in this chapter. Microwave irradiation causes KPS to break down and yield sulphate anion radicals, which pull hydrogen atoms out of hydroxyl groups of the polysaccharide units of BPS. As a result, macroradicals can initiate the radical polymerization of AcM and produce graft copolymer. The presence of MBA during radical polymerization results in the formation of a three-dimensional network. For the preparation of composite

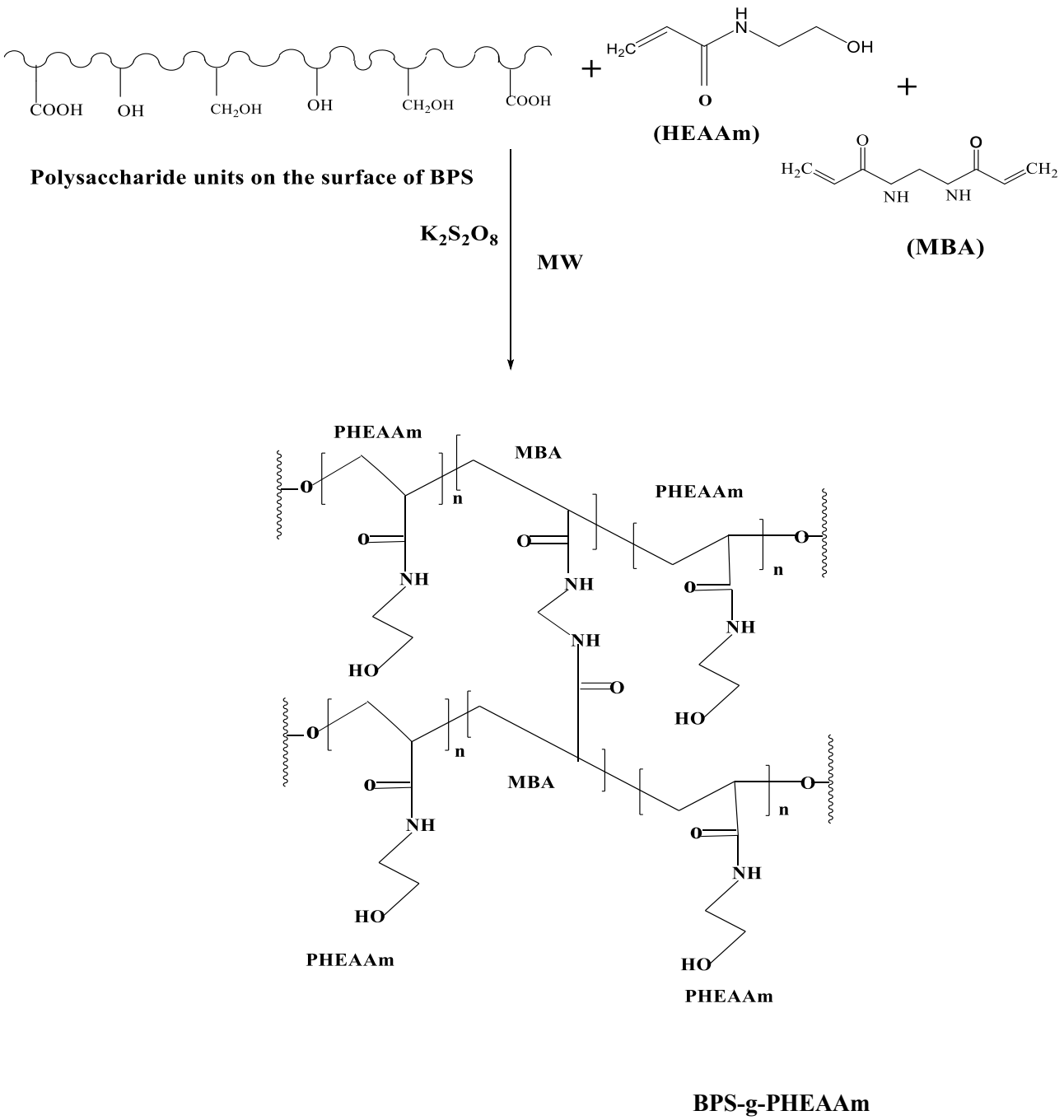
material, magnetite nanoparticles were formed within the gel network by *in situ* diffusion method. The mechanism of the formation of hydrogel and nanocomposite is shown in **Scheme 1.** FTIR, TGA, SEM, XRD and VSM techniques were used to characterize the materials. The swelling behavior of the obtained hydrogel and its nanocomposite was investigated under the pH conditions, pH=4.0, 7.1 and 9.0. The cationic dyes, MB and CV were used to examine the adsorption behavior of the gel, BPS-g-PAcM and the nanocomposite. Studies on the isotherm, kinetic, and thermodynamic aspects of dye adsorption have been carried out. The possibility of desorption in acidic solution with a pH of 1.2 was studied. The results are discussed in detail.



Scheme 1: Synthesis of BPS-g-PAcM hydrogel and BPS-g-PAcM/Fe_3O_4 nanocomposite

Chapter 4: Synthesis, characterization and dye adsorption studies of Banana Pseudo Stem supported-poly [(N-hydroxyethyl acrylamide)] graft polymer (BPS-g-PHEAAm) hydrogel and its magnetic nanocomposite

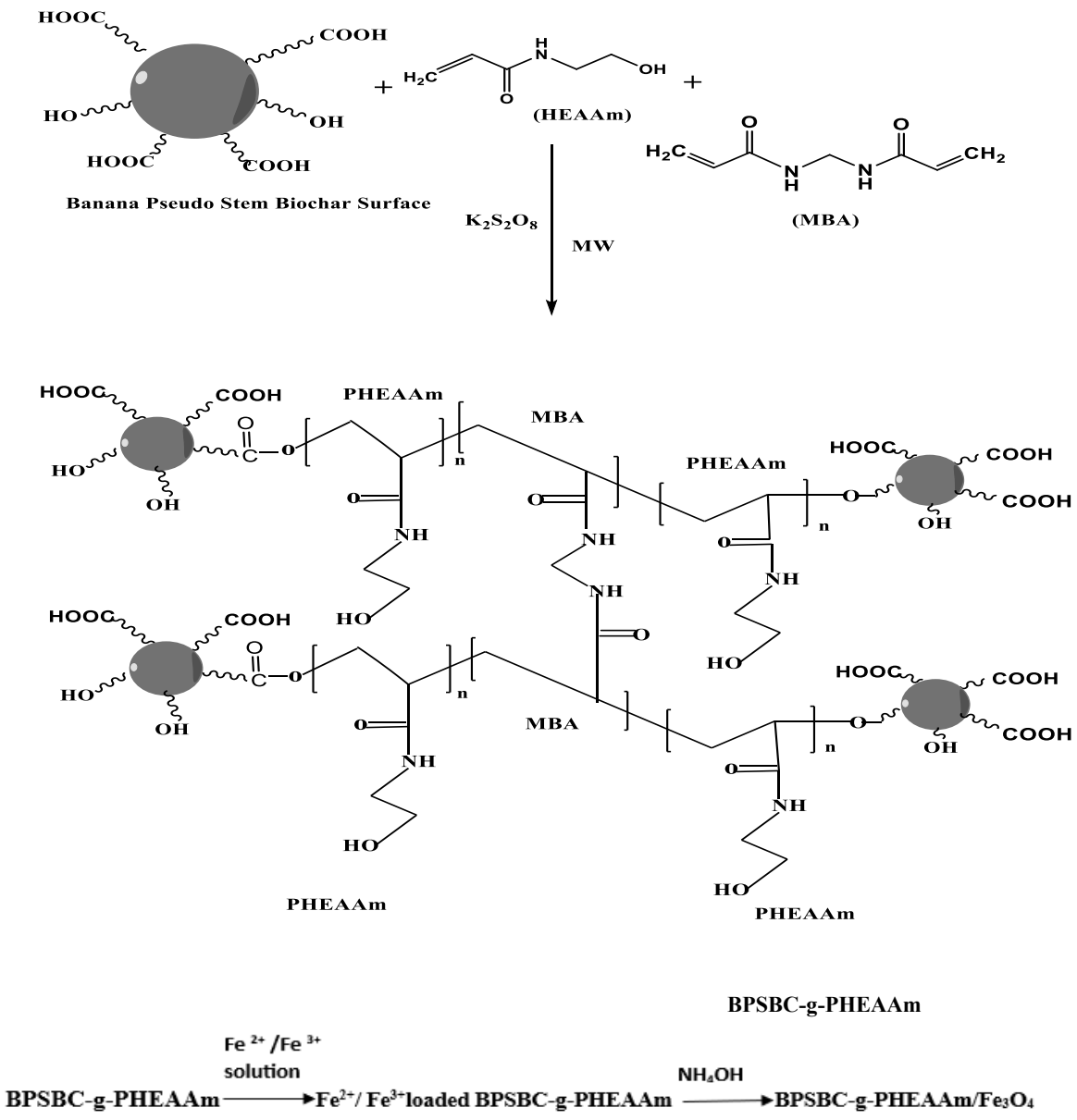
The development of Banana Pseudo Stem-graft-poly(N-hydroxyethylacrylamide) hydrogel (BPS-g-PHEAAm) and its nanocomposite with magnetite, (BPS-g-PHEAAm)/Fe_3O_4 is discussed in this chapter. In this study, Banana Pseudo Stem was functionalized with N-hydroxyethyl acrylamide and crosslinked with MBA utilizing a microwave irradiation technique to create BPS-g-PHEAAm hydrogel. For the preparation of composite material, magnetic nanoparticles were formed within the gel network by *in situ* diffusion method. **Scheme 2** depicts the various steps involved in the formation of a hydrogel and the nanocomposite. The FTIR, TGA, SEM, VSM and XRD techniques were used to characterize the samples. The swelling study was carried out under the pH conditions, pH 4.0, 7.1 and 9.0. The cationic dyes, MB and CV were used in the adsorption studies. The isotherm, kinetic, and thermodynamic aspects of adsorption have been studied. Desorption studies have been performed to test the possible recovery of adsorption material for reuse. The results have been discussed.



Scheme 2: Synthesis of BPS-g-PHEAAm hydrogel and BPS-g-PHEAAm/Fe_3O_4 nanocomposite.

Chapter-5: Synthesis, characterization, and dye adsorption studies of Banana Pseudo Stem derived Biochar-graft-poly [(N-hydroxyethylacrylamide)] (BPSBC-g-PHEAAm) hydrogel its magnetic nanocomposite

This chapter deals with the work related to development of an adsorbent material made by functionalizing the char obtained from BPS. Banana pseudo stem was heated to 500°C in a muffle furnace. The resulting biochar was functionalised by graft polymerization with HEAAm monomer in the presence of MBA as the crosslinking agent. It is incorporated with Fe_3O_4 nanoparticles to obtain the nanocomposite (BPSBC-g-PHEAAm/Fe_3O_4). The mechanism of formation of the hydrogel and its nanocomposite is shown in **Scheme 3**. FTIR, TGA, XRD, SEM and VSM techniques were used to characterize hydrogel. The swelling behaviour of adsorbent materials in aqueous buffer solutions of pH 4.0, 7.1, and 9.0 was studied .The ability of the gel and its nanocomposite to serve as an adsorbent for the removal of dyes, MB and CV has been evaluated. The kinetic, isotherm, and thermodynamic aspects of adsorption have been studied. Studies on desorption have also been performed to confirm the reusability. Results have been discussed.

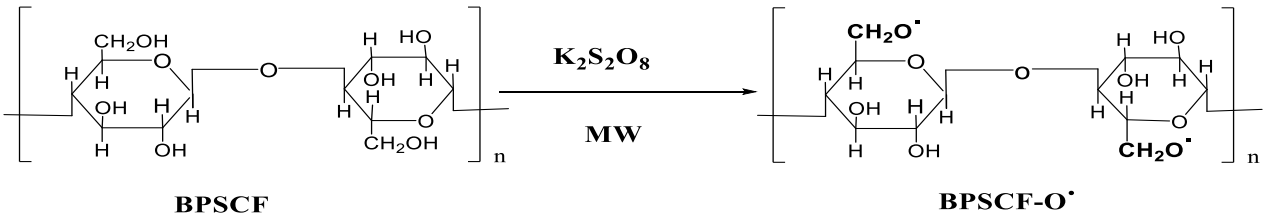


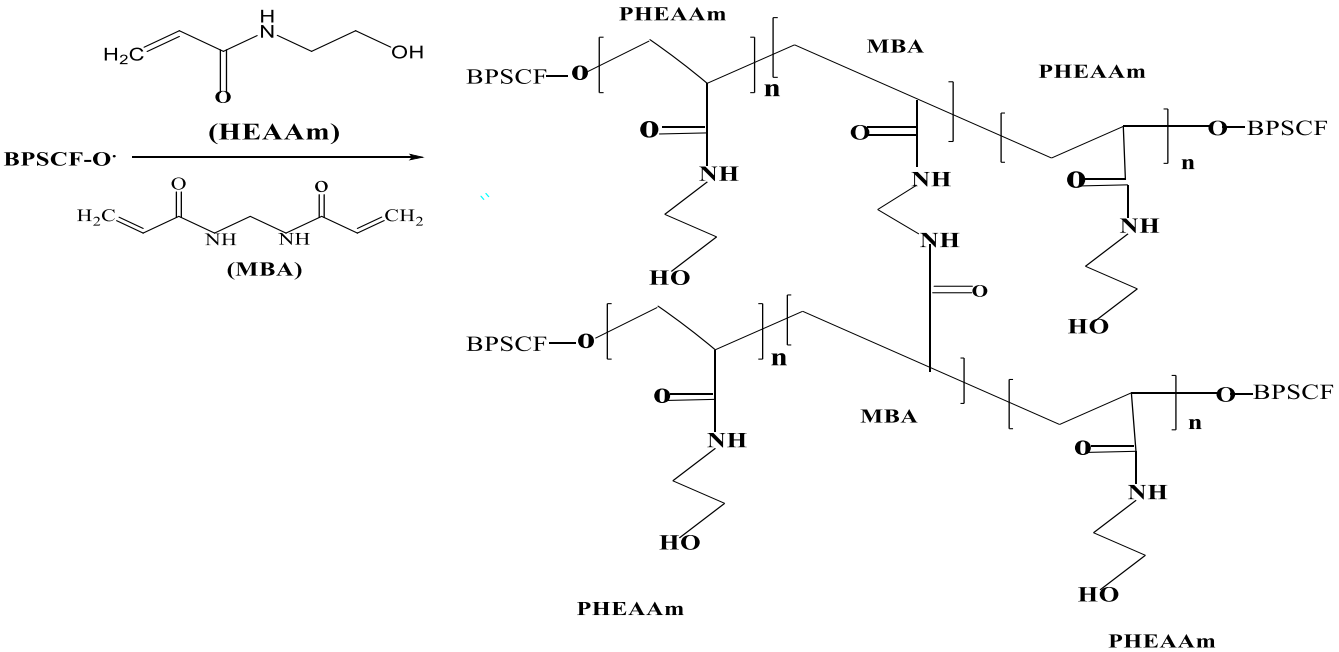
Scheme 3: Synthesis of BPSBC-g-PHEAAm hydrogel and BPSBC-g-PHEAAm/Fe_3O_4 nanocomposite

Chapter-6: Synthesis, characterization, and dye adsorption studies of Banana Pseudo Stem derived Cellulose Fiber-graft-poly [(N-hydroxyethylacrylamide)] (BPSCF-g-PHEAAm) hydrogel and its magnetic nanocomposite

This chapter discusses the preparation of the hydrogel, BPSCF-g-PHEAAm/Fe_3O_4 which is made using cellulose fibers extracted from BPS. The procedure adopted for extraction of cellulose fiber from BPS has been presented. Radical polymerization of the monomer has been attempted in the presence of HEAAm, and MBA as the crosslinker by microwave-assisted method to yield BPSCF-g-PHEAAm gel. A hybrid nanocomposite, BPSCF-g-PHEAAm/Fe_3O_4 has been developed by

incorporation of Fe_3O_4 nanoparticles. The mechanism of formation of hydrogel and nanocomposite is shown in **Scheme 4.** To characterize the materials, FTIR, TGA, XRD, SEM, and VSM techniques have been employed. The swelling behaviour of hydrogel and nanocomposites were studied under the pH conditions, pH=4.0, 7.1 and 9.0. The adsorbent samples developed were studied for removal of MB and CV from aqueous solutions. Kinetics, isotherms, and thermodynamics of adsorption process have been studied. Desorption study has also been carried out to prove the reusability of the adsorbent materials. The results have been discussed in detail.





Scheme 4: Synthesis of BPSCF-g-PHEAAm and BPSCF-g-PHEAAm/Fe_3O_4 nanocomposite

Summary and Conclusions

The characteristics of adsorbent materials made in the present work and their adsorption capacities have been compared in the present section of the thesis. A comparison has also been made with other similar materials reported in literature. The future scope of the work has been mentioned.

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Papers under communication

1. Shruthi S., & Vishalakshi B., Banana Pseudo Stem supported polymeric adsorbent material for the treatment of wastewater contaminated with dyes - Communicated to "Polymer Bulletin" (under revision).
2. Shruthi S., & Vishalakshi B., Development of Banana Pseudo Stem supported polymeric adsorbent for wastewater treatment - Communicated to "Fibers and Polymers" (under revision).
3. Shruthi S., & Vishalakshi B., Hybrid Banana Pseudo Stem Biochar and poly (N-hydroxyethyl acrylamide) hydrogel for effective dye removal from wastewater - Communicated to "Journal of Environmental Chemical Engineering" (under revision).
4. Shruthi S., & Vishalakshi B., Development of Banana Pseudo Stem based Cellulose Fiber graft polymer gel and its magnetic nanocomposite as adsorbents for dye removal from wastewater - Communicated to "Biological Macromolecules".

Papers Presented in Conferences

1. **Shruthi S**, and Vishalakshi B., "Development of Banana Pseudo Stem supported polymeric adsorbent for wastewater treatment" at Virtual International Conference on Surface Chemistry held at Annamalai University, Annamalainagar during 11-12 February 2022.
2. **Shruthi S**, and Vishalakshi B., "Banana Pseudo Stem supported polymeric adsorbent material for the treatment of wastewater contaminated with dyes" at International Conference (Hybrid mode) on Nano vision 2022-Emerging trends in Nanotechnology and Biotechnology held at Gyan Vihar University, Jaipur, Rajasthan during 19-20 April 2022.
3. **Shruthi S,** and Vishalakshi B., "Hybrid Banana Pseudo Stem Biochar and poly (N-hydroxyethyl acrylamide) hydrogel for effective dye removal from wastewater" at International Conference on

Recent Trends in Applied Sciences held at Srinivas Institute of Technology Valachil, Mangalore during 3-4 August 2022.

4. **Shruthi S,** and Vishalakshi B., "Development of Banana Pseudo Stem Cellulose Fiber based magnetic nanocomposite adsorbent for dye adsorption studies" at International Conference on Recent Trends in Applied Sciences held at Srinivas Institute of Technology Valachil, Mangalore during 26-27 September 2023 (**received best paper award**).

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